

10-
66-

**This Page Is Inserted by IFW Operations
and is not a part of the Official Record**

BEST AVAILABLE IMAGES

**Defective images within this document are accurate representations of
the original documents submitted by the applicant.**

Defects in the images may include (but are not limited to):

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORLED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

L102,463



PATENT SPECIFICATION

DRAWINGS ATTACHED

L102,463

Inventor: FREDERICK MOLYNEUX

Date of filing Complete Specification: 11 March, 1965.

Application Date: 13 Dec., 1963.

No. 49318/63.

Complete Specification Published: 7 Feb., 1968.

© Crown Copyright 1968.

Index at acceptance:—Cl. A(2B, 3D2, 3D3, B1A, B1D, C5A, D10, D45, G13) AG13D10, AG13D45

Int. Cl.—C 23 g 1/36

COMPLETE SPECIFICATION

Improvements in or relating to a process for the Treatment of Spent Acid Liquors

We, MOLBROS LIMITED, a British Company of Peveril, 42 Irby Road, Heswall, Wirral, Cheshire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to a process for the treatment of spent acid liquors and more particularly to the treatment of such liquors containing contaminating salts so as to recover and separate the acid therefrom for further use.

According to the invention there is provided a process for the recovery of an acid from a spent acid liquor solution containing an acid and a contaminating salt which comprises adding to the acid solution a chemical compound which addition can result either in the formation in the acid solution of a contaminating salt of reduced solubility as compared with the original contaminating salt or in a reduction of the solubility of the original contaminating salt, and effecting crystallisation of the salt of reduced solubility from the acid solution by evaporative cooling by passing the solution through a cooling tower containing packing counter-current to a stream of air, removing deposited salt crystals and drawing off the cooled separated acid.

For a continuous treatment the separated acid may be divided into two portions, one portion being returned to the tower together with a further quantity of treated spent liquor.

Preferably the current of air introduced into the cooling tower is dried before said introduction. Suitably the drying is effected by passing the air counter-current to a flow of concentrated sulphuric acid.

Where the spent liquor contains sulphuric acid it is convenient to mix the sulphuric acid used for the air drying step and which has become slightly diluted thereby with the recovered acid so as to fortify the latter. Such mixing can suitably be effected in a device

consisting of a finned air-cooled hydraulic cyclone mixer.

The substance to be added to form in the contaminated acid solution, a salt of reduced solubility compared with that of the original contaminant may for example be ammonium sulphate or in other cases sodium chloride or sulphuric acid. Alternatively the substance may be a synthetic detergent e.g. an anionic surface tension reducing agent at a concentration of 5% w/w in the liquor or aqueous solutions of acetone or alcohol in concentrations up to 50% w/w in the liquor which reduce the surface tension and also the solubility of the original contaminant. Ammonium sulphate and sodium chloride may be used with spent acid liquors from steel pickling process to form double salts and sulphuric acid may be used in the case of acid liquors from galvanising pickle baths or stainless steel pickling baths to regenerate the acid and deposit metal sulphate crystals.

In the accompanying drawings three different types of apparatus suitable for effecting the evaporative cooling and crystallisation in accordance with the invention are described by way of illustration wherein,

Figure 1 is a diagrammatic illustration of an assembly of apparatus for recovery of sulphuric acid from spent acid pickling liquor in accordance with the process of the present invention,

Figure 2 is a diagrammatic illustration of a second assembly of apparatus for the recovery of sulphuric acid in accordance with the process of the present invention,

Figure 3 is a fragmental view of a type of plastics packing used in cooling towers of the apparatus,

Figure 4 is a diagrammatic illustration in front elevation of a third assembly of apparatus suitable for the recovery of hydrochloric acid from steel pickling spent liquor in accordance with the process of the present invention and

[Pri.

Figure 5 is a side elevation of the apparatus as shown in Figure 4.

In the apparatus illustrated in Figure 1, 10 is a vortex mixing device into which is fed through feed pipe 11 the spent acid pickling liquor. From a container 12 ammonium sulphate is fed through a flow control feed 13 to the mixing device 10. From the mixing device 10 the treated acid liquor is passed by inlet 14 into a collector 15, whence it is transferred by a glandless submersible pump 16 through conduit 17 to the cooling tower 18. The cooling tower 18 is provided with an entrainment mist separator 19 and distributor plate 20. A blower 21 feeds air through pipe 22 to the tower 18 counter-current to the flow of acid liquid. Crystals of the contaminant salt, now present as FeSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $6\text{H}_2\text{O}$, are received in the basin 23 and are removed at 24 whilst the recovered liquor is drawn off via conduit 25. The packing in the tower consists of an assembly of corrugated polyvinyl chloride sheets 26 arranged as shown in Figure 3.

In the assembly of apparatus illustrated in Figure 2 there is provided a mixing device 31, an agitator 32, an inlet 33 for the acid liquor, a supply hopper 34 for the added compound (ammonium sulphate crystals). Mixing of the added compound with the spent acid liquor is effected in compartment 31a and from compartment 31b the treated acid liquor is pumped by submersible pump 35 through a conduit 36 which feeds the treated acid liquor to the top of a cooling tower 37, provided with a mist entrainment separator 38 and distributor plate 39. A sump 40 is provided for the deposited crystals and recovered acid from which some of the recovered acid is pumped by pump 42 through conduit 41 to the top of cooling tower 37. Air is led to the cooling tower 37 from blower 43 through pipe 44, drying tower 45 and pipe 46. In the drying tower 45, which is ring packed, concentrated sulphuric acid is directed counter-current to the air, being fed from inlet 47 into basin 48 and pumped from there by pump 49 through conduit 50 to the top of tower 45. Some concentrated acid is directed through conduits 50 and 51 to a finned air-cooled hydraulic cyclone mixer 52. That part of the recovered acid which is not re-cycled through the cooling tower 37 via conduit 41 is drawn-off through the conduit 53 and passes into the finned air-cooled hydraulic cyclone mixer 52. Acid which has passed through the drying tower 45 is returned to the basin 48 and recirculated by pump 49. In the cyclone mixer 52 the recovered acid is mixed with the concentrated acid and the fortified recovered acid lead away through conduit 54. Crystals deposited in the sump 40 are removed via outlet 55. The cooling tower 37 may be provided with packing 26 of the kind illustrated in Figure 3.

Apparatus for recovery of hydrochloric acid from a mixture of hydrochloric acid and ferrous chloride is illustrated in Figures 4 and 5. In this apparatus spent acid liquor is fed through an inlet 60 where it is mixed in cyclone mixer 61 with sulphuric acid fed via inlet 62 and from there the treated acid liquor passes through inlet 63 to the cooling tower 64 which is provided with corrugated P.V.C. sheet packing 65 of alternate horizontal and vertical layers. The cooling tower 64 is also fitted with a mist entrainment separator 66 and distributor plate 67. Cooling air enters the cooling tower 64 from the axial flow fan 68 and passes counter-current to the acid liquor. Acid liquor and crystals collect in the sump 69, deposited crystals being withdrawn via the outlet 70, the recovered acid liquid being drawn off by pump 71 through conduit 72. One portion of this recovered acid liquor is drawn off via outlet 73 and the remainder re-cycled to the tower 64 via conduit 74.

The liquid distributor plate in the various embodiments conveniently consists of a tray of plastics material, the base of the tray being of grid-like form. The acid mist entrainer is suitably also made from synthetic plastics material or of glass. This may suitably consist of closely spaced inclined glass plates or synthetic plastics material or of cylindrical rods closely spaced or alternatively may be of loosely woven glass fibre.

The synthetic plastics material employed for the tower, for the distributor plate, for the collection sumps and for the pumps may suitably be of rigid polyvinyl chloride material. The conduits or pipe lines are preferably formed from polythene and the cooling tower packing is suitably of corrugated flexible polyvinyl chloride sheeting.

The finned air-cooled cyclone mixer may conveniently be of copper, stainless steel or "Monel" metal ("Monel" is a Registered Trade Mark) with or without a synthetic plastic lining.

The process in accordance with the invention is particularly suitable for example for the recovery of sulphuric acid from an acid pickling liquor. Such a liquor consisting of 6% sulphuric acid and 15% ferrous sulphate at a temperature of 60 to 70°C is fed into the mixing basin 31 of the apparatus illustrated in Figure 2, this being of a size capable of dealing with an input of 2,000 gallons per hour into which mixing basin 31 there is also introduced crystals of ammonium sulphate from a supply hopper 34. The mixture of acid liquor and ammonium sulphate is then pumped to the top of the cooling tower 37 where it passes downwardly through the distributor plate 39 and the packing of plastics material counter-current to a flow of air supplied by the blower 43, after the air has been dried by contact with a counter-current flow of sulphuric acid of 98% concentration. The

cooled liquid with deposited crystals of ferrous ammonium sulphate falls into a collecting sump 40 from which the collected crystals are removed. The cooled separated liquid is then removed by means of the submersible pump 42 suitably of synthetic plastics material, part of this recovered acid being re-cycled into the cooling tower 37 and part being fed to a finned air-cooled hydraulic cyclone mixer 52 at the exit from the drying tower where it is mixed with the concentrated acid used for drying the air. The recovered separated acid of approximately 10% concentration is thus fortified by mixing with the concentrated acid to give a final concentration of approximately 15%. When dried air is employed the percentage removal of ferrous sulphate is about 90 to 95% but only 60 to 65% when the air is not dried, as for example in the apparatus illustrated in Figure 1.

The apparatus illustrated in Figures 4 and 5 is as stated suitable for the treatment of spent acid liquors consisting of hydrochloric acid and ferrous chloride, this acid solution being treated with sulphuric acid to bring about the desired reduction of solubility of a contaminating salt.

The invention is applicable generally to the treatment of spent liquors from steel pickling baths where ferrous salts as well as sulphuric acid and hydrochloric acid are concerned, from galvanising pickle baths where liquors containing hydrochloric acid and ferrous chloride are concerned and from stainless steel pickling baths where nitric acid, hydrofluoric acid and iron, chrome and nickel salts are present in the spent liquor.

WHAT WE CLAIM IS:—

1. A process for the recovery of an acid from a spent acid liquor solution containing an acid and a contaminating salt which comprises adding to the acid solution a chemical compound which addition can result either in the formation in the acid solution of a contaminating salt of reduced solubility as compared with the original contaminating salt or in a reduction of the solubility of the original contaminating salt and effecting crystallisation of the salt of reduced solubility from the acid

solution by evaporative cooling by passing the solution through a cooling tower containing packing counter-current to a stream of air, removing deposited salt crystals and drawing off the cooled separated acid.

2. A process in accordance with claim 1 wherein the cooling tower packing is of synthetic plastics material.

3. A continuous process for the recovery of an acid from a spent acid liquor containing an acid and a salt in accordance with claim 1 or claim 2 wherein the separated acid drawn off is divided into two portions, one portion being returned through the cooling tower together with a further quantity of spent liquor.

4. A process for the recovery of an acid in accordance with any of the preceding claims wherein the current of air introduced into the cooling tower is dried before said introduction.

5. A process in accordance with claim 4 wherein the drying is effected by passing the air in counter-current to a flow of concentrated sulphuric acid.

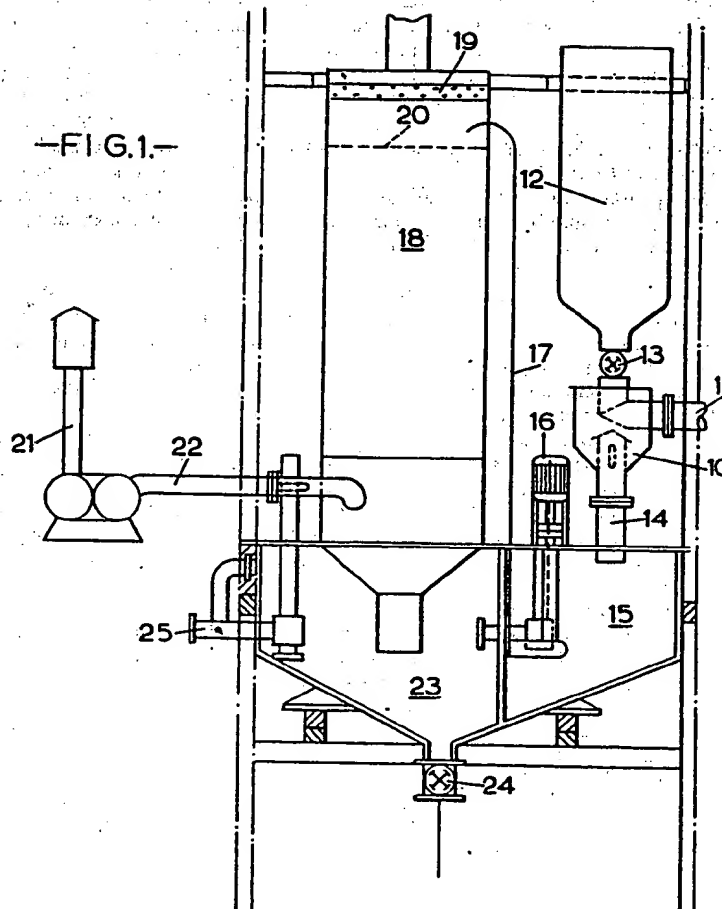
6. A process for the recovery of an acid from a spent acid liquid containing sulphuric acid in accordance with claim 5 wherein the sulphuric acid used for the air-drying step is subsequently mixed with the acid recovered from the spent liquor so as to fortify the recovered acid.

7. A process in accordance with any of the preceding claims wherein the chemical compound added to provide reduced solubility of a contaminating salt in the acid of the spent liquor is ammonium sulphate, sodium chloride, sulphuric acid, an anionic surface tension reducing agent at a concentration of 5% w/w in the liquor, or aqueous solutions of acetone or alcohol in concentrations up to 50% w/w in the liquor.

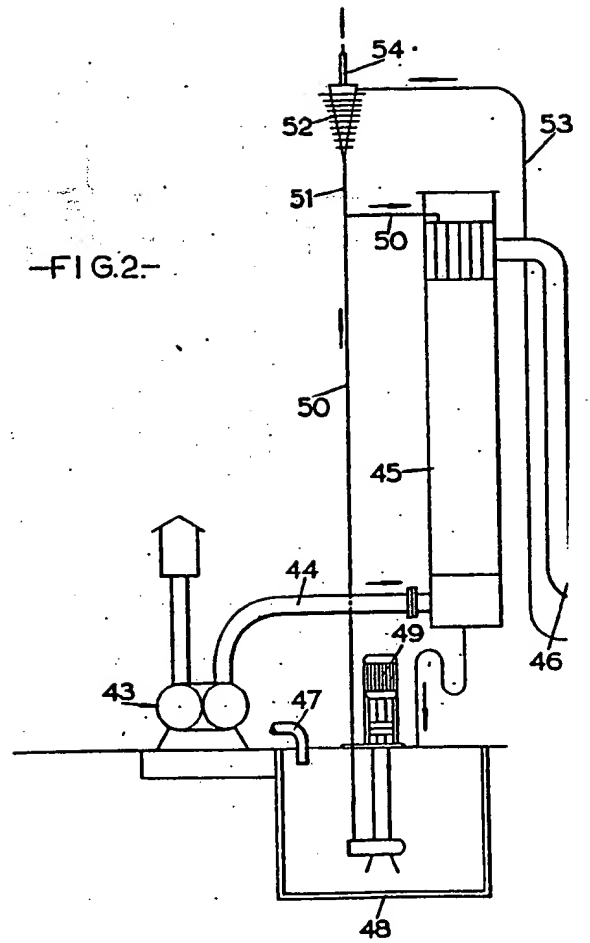
8. A process for the recovery of an acid from a spent acid liquid containing an acid and a salt substantially as herein described.

E. R. ROYSTON & CO.,
Agents for the Applicants,
Chartered Patent Agents,
Tower Building,
Water Street, Liverpool, 3.

-FIG.1-

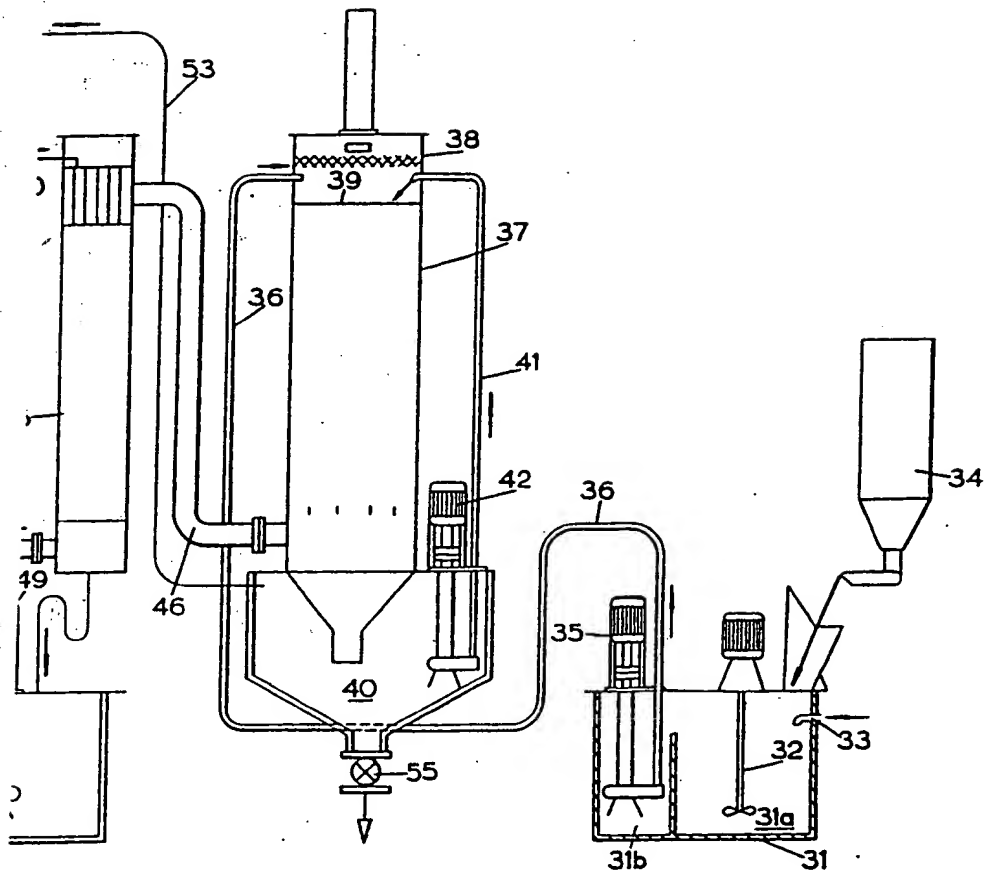


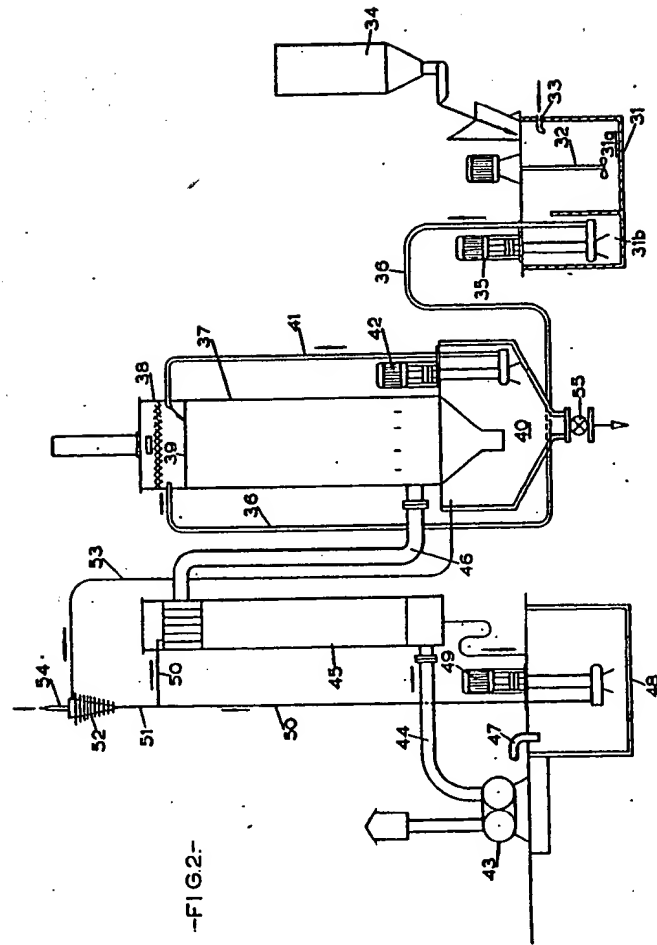
-FIG.2-



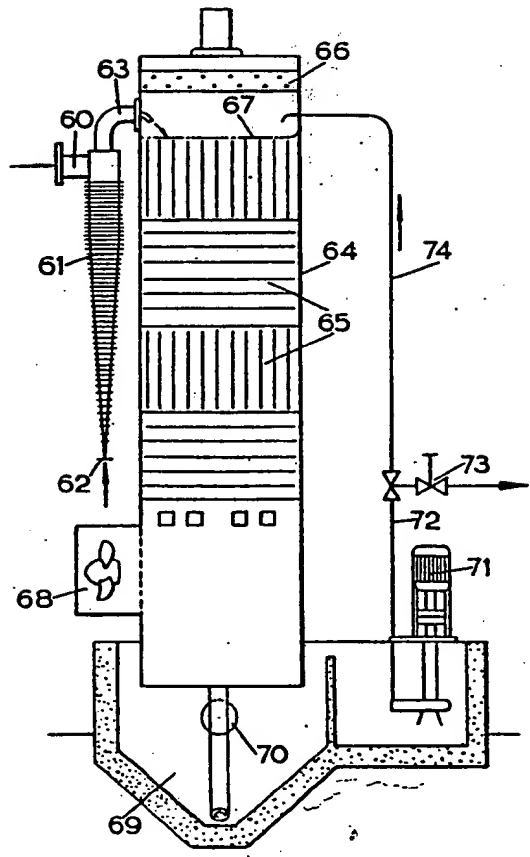
1102463 COMPLETE SPECIFICATION

3 SHEETS This drawing is a reproduction of
the Original on a reduced scale
Sheet 2





-FIG. 4-



1102463

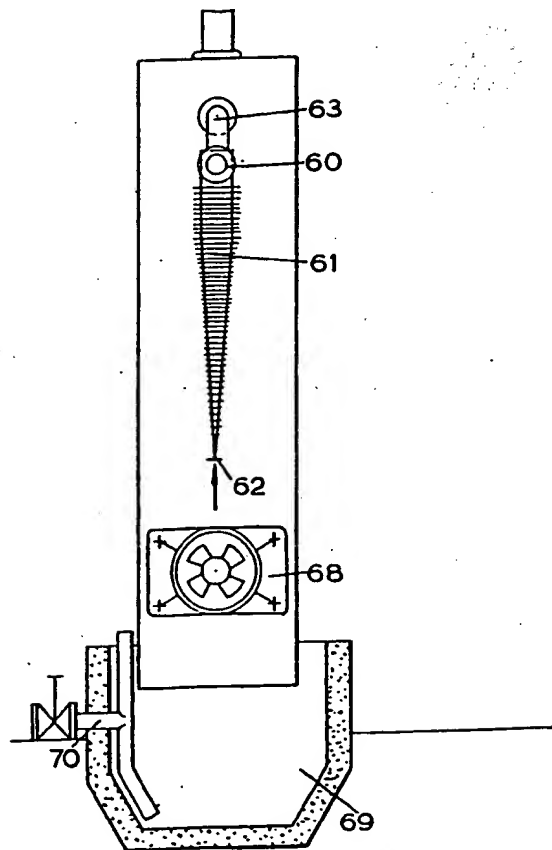
COMPLETE SPECIFICATION

3 SHEETS

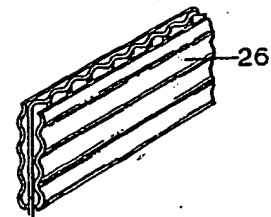
*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 3

-FIG.5-



-FIG.3-



1102463 COMPLETE SPECIFICATION
 3 SHEETS
 This drawing is a reproduction of
 the Original on a reduced scale
 Sheet 3

FIG. 3.

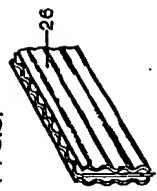


FIG. 4.

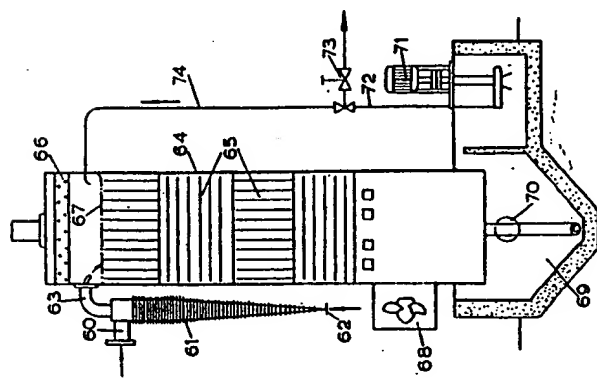


FIG. 5.

